EVALUATION STUDY ABOUT SYNTHETIC NATURAL GAS

By

Mohd Elmie Farhan Bin Abd Wahab

Dissertation submitted in partial fulfillment of
the requirements for the Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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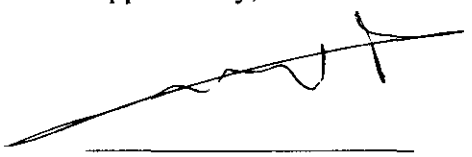
Approved by,



(Dr. Usama Mohamed Nour)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHD ELMIE FARHAN BIN ABD WAHAB

ABSTRACT

Today, natural gas is an important part of energy supply with electricity and for covering heat demand. Natural gas consumption, however, rises steadily all over the world, so that it is conceivable that there will be (just like with crude oil) a noticeable shortage and dramatic price increases in the medium term. Increasing demand for natural gas and high natural gas prices in the recent past has led many to pursue unconventional methods of natural gas production. Natural gas that can be produced from coal or biomass is known as "synthetic natural gas" or "substitute natural gas" (SNG). SNG is a manufactured form of natural gas. Substitution of natural gas from renewable resources is therefore a necessity not only due to ecological reasons but also for economic reasons.

ACKNOWLEDGEMENT

First and foremost, I would like to praise Allah the Almighty for with His blessings and guidance I am able to successfully finish my dissertation report.

My heartily gratitude goes to my Final Year Project Supervisor, Dr Usama Mohamed Nour for the project plans, and also for the knowledge and experiences shared. His guidance had developed my interest in this topic and make me clear what I have should do in order to achieve the target. Heartfelt appreciation is given to University Technology PETRONAS (UTP) and Chemical Engineering Department for equipping students with essential skills and excellent theoretical as well as practical work. I would like to raise many thanks to Dr. Khalik bin Mohd Sabil, for being my final year project coordinator and keeping the supervision in great control. Finally, my acknowledgement is considered incomplete without thanking all my fellow colleagues, friends and family who have been giving great support and encouragement for me to complete this final report/ dissertation.

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CHAPTER 1: PROJECT BACKGROUND

1.1 Problem Statement

Energy demand is increasing across the globe. Increasing consumption and the resultant increasing price of natural gas are a concern. According to DOE (2008), 90% of new U.S. power plants will be natural gas–fired plants. In the Netherlands annually almost 3,300 PJ of primary energy is consumed for the production of electricity, heat, transportation fuels, and chemicals and other products. Natural gas consumption represents almost 46% of this Dutch (primary) energy consumption. The main applications of natural gas are chemistry, power production, and – by far the largest – the production of heat for both households and industry. The substitution of natural gas by a renewable equivalent is an interesting option to reduce the use of fossil fuels and the accompanying greenhouse gas emissions, as well as from the point of view of security of supply. Via this route can be benefited from all the advantages of natural gas, like the existing dense infrastructure, trade and supply network, and natural gas applications.

1.2 Objectives

The main objective of the project is to evaluate the synthetic natural gas from biomass. Plus, there are additional objectives those runs parallel which are:

- Evaluation of the existing technology of synthetic natural gas focusing on Methanation process.
- Enhancement of the existing technology regarding the gas quality (modeling).
- Modeling and simulation of the existing technology.

1.3 Scope of Study

The project is divided into three phases in order to achieve the objectives. Firstly, the background of Synthetic Natural Gas is studied. The objectives, methodology and current technologies as well as implementation are identified and understood. Next phase is to prepare the process diagram in producing SNG in Process Flow Diagram (PFD) format. The process will be simulated by using Hysis in order to identify whether the flow is relevant or not. In this simulation process, any modification of the process will be applied in order to optimize the production. The final phase is the evaluation and presentation of the result achieved during the simulation.

1.4 Background of Study

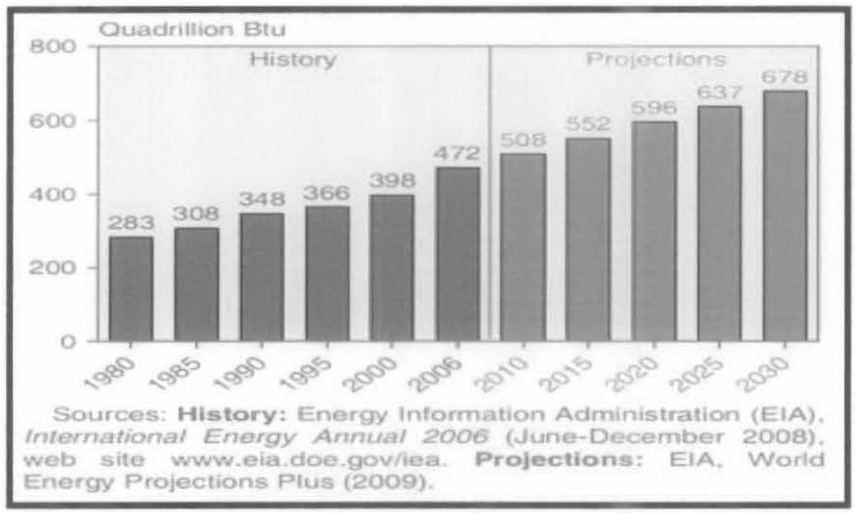

Figure 1 : World Market Energy Consumption

Based on International Energy Outlook 2009 (IEO2009) projection, the total amount energy consumption is projected to increase about 44% from 2006 to 2030. The amount of the world energy consumption increases from 472 quadrillion Btu in 2006 to 552 quadrillion Btu in 2015 and 678 quadrillion Btu in 2030 as shown in figure 1 above. The consumption of energy is proportional to the world energy demand. From year to year the energy demand is increase historically so that we can predict the amount of energy demand will increase significantly. The use of all energy sources increases over the time frame of the *IEO2009* reference case as shown in figure 2 below. Renewable sources of energy are the fastest-growing source of world energy, with consumption increasing by 3.0 percent per year. Natural gas is one of the important sources of energy for electricity generation worldwide, because it is more efficient and less carbon-intensive than other fossil fuels like coal and oil shale.

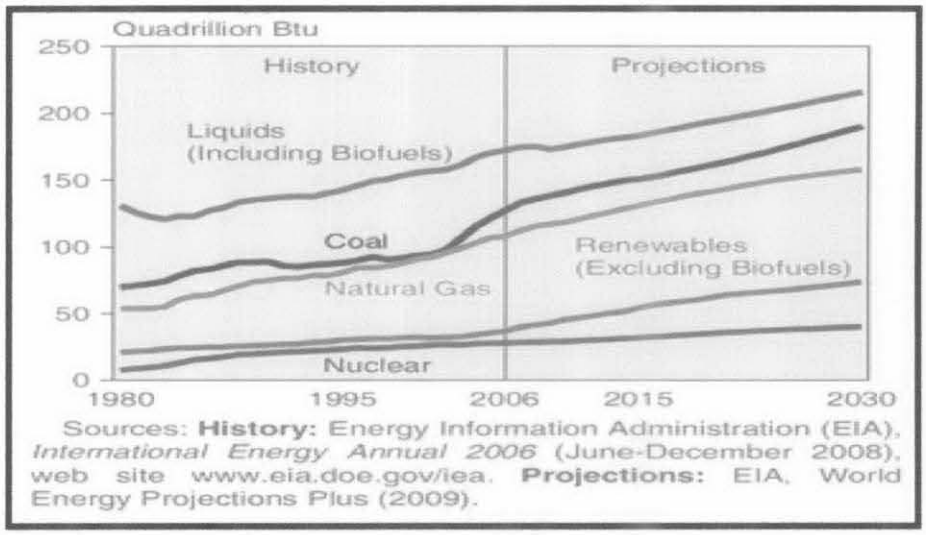

Figure 2: World Market Energy Use by Fuel Type

According to figure above, the total natural gas consumption increases by 1.6 percent per year on average, from 104 trillion cubic feet in 2006 to 153 trillion cubic feet in 2030, and its use in the electric power sector increases by 2.1 percent per year. With world oil prices assumed to rebound following the current economic downturn and then rise through 2030, consumers are expected to choose less expensive natural gas to meet their energy needs whenever possible, particularly in the industrial sector, where, for example, newly constructed petrochemical plants are expected to rely increasingly on natural gas as a feedstock. As the demand increase and the natural gas from nonrenewable source which is from petroleum well become depleted, so that production of synthetic natural gas from renewable sources like biomass in bigger scale is necessary.

Biomass has been a major source of energy throughout the world since the beginning of civilization. Biomass is the primary source of energy for nearly 50% of the world's population and wood biomass is a major renewable energy source in the developing world, representing a significant proportion of the rural energy supply. On several years back, the number of countries use biomass as an alternative source of

energy has increased rapidly, and has helped make biomass an attractive and promising option in comparison to other renewable energy sources. The global use of biomass for energy increases continuously and has doubled in the last 40 years as shown in the figure 3 below. This according to the World Bank (2009) who uses IEA electronic files. Biomass can be used in several fields such as heat, power, liquid biofuels and biobased products and also producing synthetic natural gas. Contribution of biomass to the global energy demand of 470 EJ in 2007 is only 10%, mainly in the form of traditional non-commercial biomass. Moreover, we know that biomass can be used to produce different forms of energy, thus providing all the energy services required in a modern society. Furthermore, compared to other renewable, biomass is one of the most common and widespread resources in the world. Thus, biomass has the potential to be a source of renewable energy, both locally and in large parts of the world. Worldwide, biomass is the fourth largest energy resource after coal, oil, and natural gas - estimated at about 10% of global primary energy.

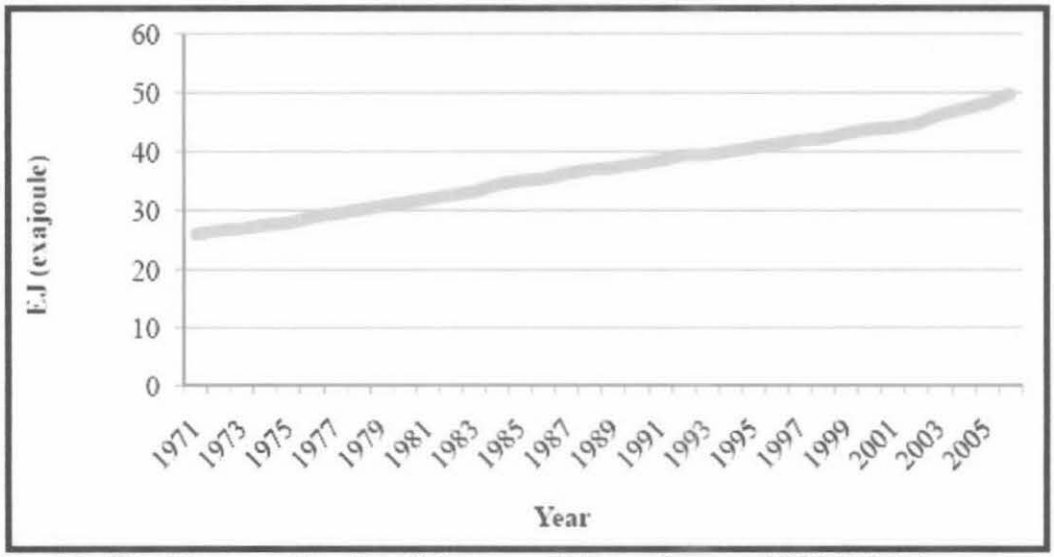

Figure 3: World use as Combustible renewables and waste 1971-2006 (source: world bank, 2009)

CHAPTER 2: LITERATURE REVIEW AND THEORY

2.1 Synthetic Natural Gas

Synthetic Natural Gas (SNG) is a natural gas that is generated or produced from the carbonaceous stock like biomass and also coal. SNG also known as "Subtitute Natural Gas" can be manufactured as natural gas from petroleum reservoir. The substitution of natural gas by a renewable equivalent is an interesting option to reduce the use of fossil fuels and the accompanying greenhouse gas emissions, as well as from the point of view of security of supply.

According to Synthetic Fuels Handbook by James G. Speight natural gas is a gaseous fossil fuel primarily contains methane but including significant quantities of ethane, butane, propane, carbon dioxide, nitrogen, helium, and hydrogen sulfide. Natural gas from the reservoir must undergo refining process to remove almost all materials other than methane. Natural gas is colorless in its pure form and its combustible mixture of hydrocarbon gases.

According to German Energy Agency, there are a lot of benefits that we got from producing SNG from biomass. One of the benefits is the methane produced will protects our world. The methane extracted from biomass can replace fossil-based natural gas. It can in this way abate the emissions from green house gases, and thus achieve an important contribution to a sustainable and environmentally friendly energy economy. CO2 emissions resulting from the burning of fossil-based energy sources are known to be a primary cause of global warming. Natural energy sources like methane release only

as much CO2 as it's absorbed from the atmosphere by plants. Thereby, the ideal circumstances of climate-neutral energy consumption become conceivable.

The versatility of methane produced from biomass is another benefit in which it has the ability to be injected directly into the existing natural gas grid. This would increase the efficiency energy transport and also reducing the cost of transport. This methane can be used to generate electricity and heating from within smaller decentralized, or large centrally-located combined heat and power plants. It can be used by heating systems with a highly efficient fuel value, and employed as a regenerative power source in gas-powered vehicles. The utilization of this methane as a source of energy is a crucial step toward a sustainable energy supply.

2.2 Biomass

SNG that we focus on throughout this report is SNG that produced from biomass. According to Synthetic Fuels Handbook by James G. Speight, biomass refers to living and recently dead biologic material which can be used as fuel or for industrial production. For example, manure, garden waste, wood, and crop residues are all source of biomass. Biomass is renewable energy source, unlike other resources such petroleum, natural gas, tar sand, bitumen, coal and oil shale. But, like coal and petroleum, biomass is a form of stored solar energy. According to Biofuels For Transport by Worldwatch Institute, biomass feedstock can be grouped into 2 basic catagories: the current available 'first-generation' feedstock, which are harvested for their sugar, starch and oil content. Meanwhile, the second group of biomasss is known as 'next-generation' feedstock, which are harvested for their total biomass and whose fibres can only be converted into SNG by advanced technical process. The example of feedstock as follow:

Table 1: Type of Biomass Feedstock

First-Generation Feedstock	Next-Generation Feedstock
1. **Sugar Crops** ▪ ***Sugar Cane, Sugar Beet, Sweet Sorghum.*** 2. **Starch Crops** ▪ ***Corn, Wheat, Cassava, Sorghum grain,*** 3. **Oilseed Crops** ***Rapeseed, Soybean, Cottonseed, Peanut, Sunflower seed, Palam kernel, Copra, Jatropha***	1. **Cellulosic Biomass** ▪ *Wood, Tall grasses and forestry.* 2. **Biomass residues and Organic Waste** ▪ *Municipal Solid Waste, Crop Residues, Wood Residue.*

Cellulosic biomass such as wood. Tall grasses and forestry and crop residue are expected to significantly expand the quantities and types of biomass feedstock available for SNG production in the future as new conversion technologies are developed that enable the production of SNG from this feedstock. There are several reasons why cellulosic biomass is considered an attractive option. The use of waste biomass offers a way of creating value for society, displacing fossil fuel with material that typically would otherwise decompose, with no additional land use required for its production. Cellulosic biomass from fast growing perennial energy-crops, such as short rotation woody crops and tall grass crops, can be grown on much wider range of soil type, where the extensive root systems that remain in place with these crops help to prevent erosion and increased carbon storage in soil. Cellulosic biomass is difficult to break down but this tenacity of material also make it more robust in handling in which fewer costs needed to maintain the quality of the feedstock compared to many food crop. In addition, cellulosic biomass can be easier to sore for long period time, with less deterioration than sugar based feedstock.

Cellulosic biomass has three(3) primary component which are cellulose, hemicelluloses and lignin. Cellulose has the strong molecular structure made from long chain of glucose molecules with six atom of carbon per molecule. Hemicellulose is relatively a amorphous component that is easier to brakedown with chemical and heat than cellulose; it contains a mix of six-carbon(C-6) and with five-carbon (C-5) sugars. Lignin is essentially the glue that provide the overall rigidity to the structure of plants and trees. To acknowledge the mix of components, cellulosic biomass is often referred to as 'lignocellulosic' biomass and for example is wood.

Table 2: Physical composition of selected biomass feedstock

Feedstock	*Percentage (%)*		
	Cellulose	*Hemicellulose*	*Lignin*
Poplar (hybrid)	42-56	18-25	21-23
Switchgrass	44-51	42-50	13-20
Bamboo	41-49	24-28	24-26
Sugarcane Bagasse	32-48	19-24	23-32
Hardwood	45	30	20
Sofwood	42	214	26
Corn Stover	35	28	16-21
Sweet Sorghum	27	25	11

2.2.1 Cellulose

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units. Cellulose is the structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Some species of bacteria secrete it to form biofilms. Cellulose is the most common organic compound on Earth. About 33 percent of all plant matter is cellulose (the cellulose content of cotton is 90 percent and that of wood is 50 percent). Cellulose is derived from D-glucose units, which condense through β(1→4)-glycosidic bonds. This linkage motif contrasts with that for α(1→4)-glycosidic bonds present in starch, glycogen, and other carbohydrates. Cellulose is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen molecules on the same or on a neighbor chain, holding the chains firmly together side-by-side and forming *microfibrils* with high

tensile strength. This strength is important in cell walls, where the microfibrils are meshed into a carbohydrate *matrix*, conferring rigidity to plant cells.

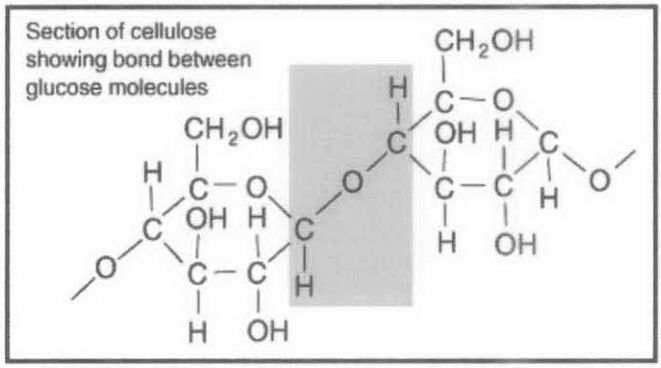

Figure 4: Molecular Structure of Cellulose

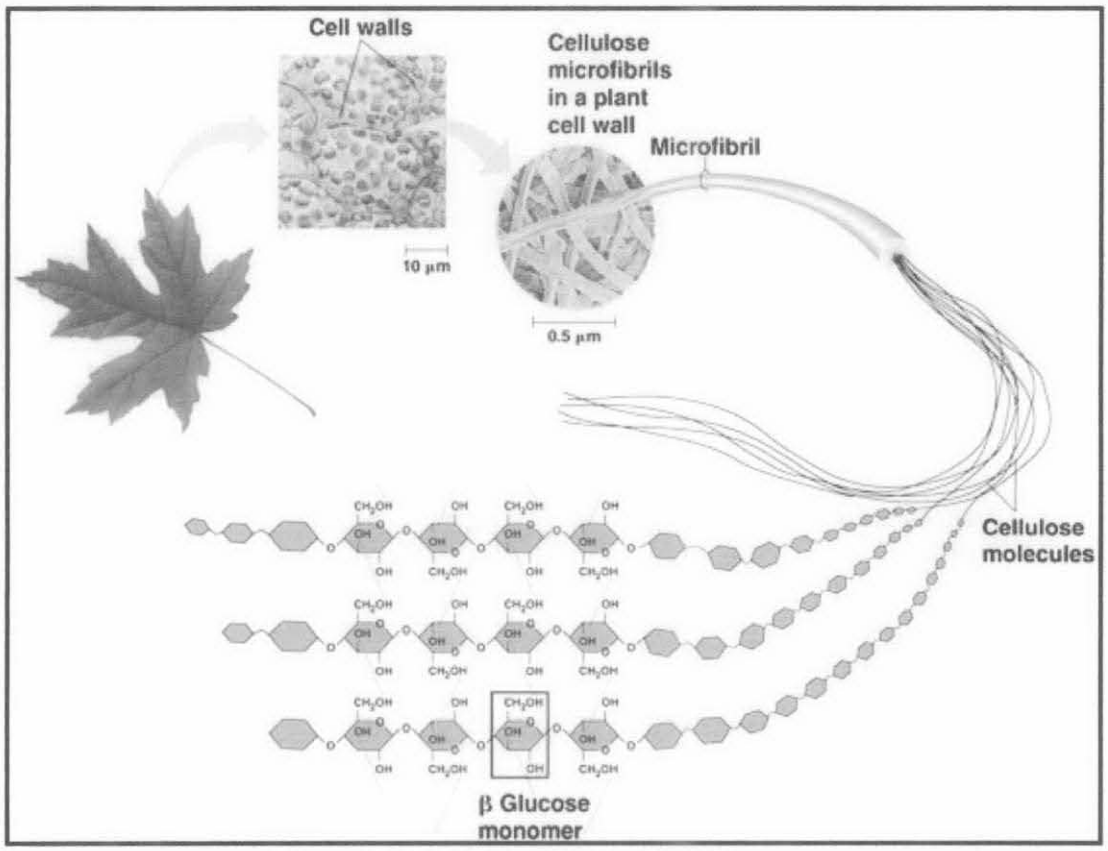

Figure 5: Cellulose, plant cell walls

2.2.2 Hemicellulose

A hemicellulose can be any of several heteropolymers (matrix polysaccharides), such as arabinoxylans present in almost all plant cell walls along with cellulose. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulose enzymes. Hemicellulose contains many different sugar monomers. In contrast, cellulose contains only anhydrous glucose. For instance, besides glucose, sugar monomers in hemicellulose can include xylose, mannose, galactose, rhamnose, and arabinose. Unlike cellulose, hemicellulose (also a polysaccharide) consists of shorter chains around 500-3,000 sugar units as opposed to 7,000 - 15,000 glucose molecules per polymer seen in cellulose. In addition, hemicellulose is a branched polymer, while cellulose is unbranched. Microfibrils are cross-linked together by Hemicellulose homopolymers. Lignins assist and strengthen the attachment of Hemicelluloses to microfibrils.

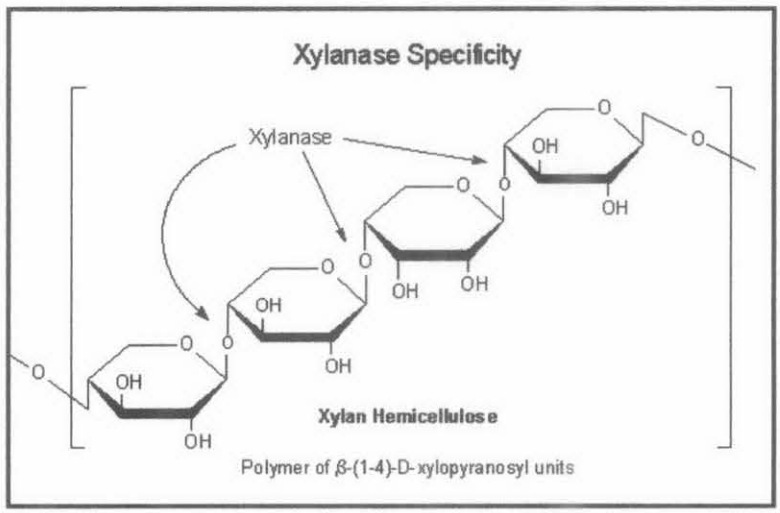

Figure 6: Molecular Structure of Hemicellulose

2.2.3 Lignin

Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components, especially in tracheids, sclereids and xylem. It is covalently linked to hemicellulose and thereby crosslinks different plant polysaccharides, conferring mechanical strength to the cell wall and by extension the plant as a whole. It is particularly abundant in compression wood but scarce in tension wood. Lignin plays a crucial part in conducting water in plant stems. The polysaccharide components of plant cell walls are highly hydrophilic and thus permeable to water, whereas lignin is more hydrophobic. The crosslinking of polysaccharides by lignin is an obstacle for water absorption to the cell wall. Thus, lignin makes it possible for the plant's vascular tissue to conduct water efficiently. Lignin is a cross-linked racemic macromolecule with molecular masses in excess of 10,000 u. The degree of polymerisation in nature is difficult to measure, since it is fragmented during extraction and the molecule consists of various types of substructures which appear to repeat in a haphazard manner. Different types of lignin have been described depending on the means of isolation.

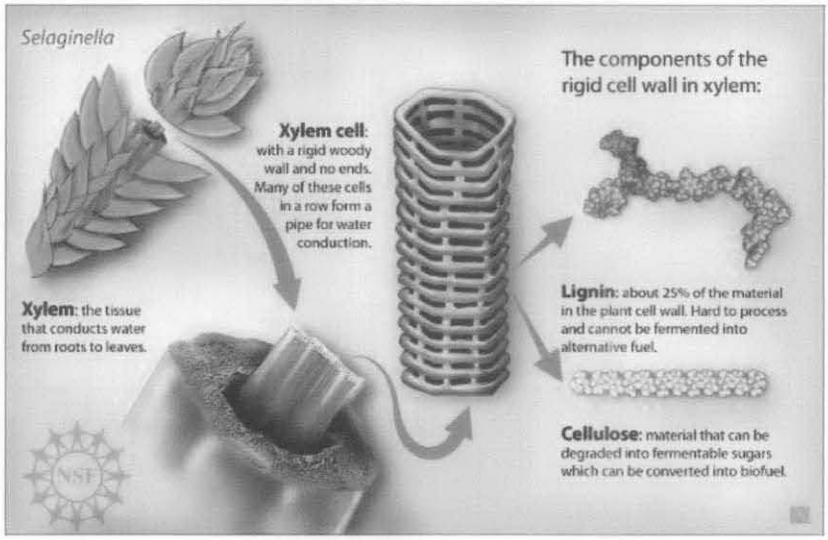

Figure 7: Structure of Selaginella

In addition to such material applications, biomass will also play an important role in the future realization of a sustainable energy system, and will be of particular

importance to the provision of heat, electricity and fuel. One of the most auspicious applications of biomass is the generation of SNG or methane precisely. The methane from biomass stabilizes the energy system. The supply of the methane can be maintained year-round. Slurry, manure and organic waste resulting from food processing continue to accumulate. Similarly, harvested biomass is stored in silos designed to be large enough to maintain the necessary supply of energy from biogas throughout the year. Thus, the production of SNG and methane especially makes an important contribution to a stable and reliable energy supply. The regularity of supply has the ability to balance the fluctuating electricity production originating from alternative renewable energy sources such as wind and solar. This advantage is increased by the ability to inject the gas directly into the existing natural gas grid and to use it independently from its production location.

For this project, the biomass properties are as below:

Table 3: Biomass properties

Type of biomass	Lignocellulosic Biomass (Wood)	
Composition	%	30% C; 47% H; 22% O; 1.1E^{-4}% N
Pressure	Bar	1.0
Temperature	^{o}C	25.0
Flowrate	Kgs^{-1}	1.1

2.3 General process of SNG production

SNG can be produced from renewable and non renewable resources such as peat, coal and biomass like wood, crops, animal dung, and also industrial and agriculture waste. Many research and study have been done in producing SNG from biomass. The SNG also been produced starting from several years back but the production is only in small quantity. I have done some reading and studies from journals and also books about the production of SNG from biomass. There are few path of producing natural gas but the basis of route to produce SNG still the same. The basic path of process or route of process to produce SNG as below:

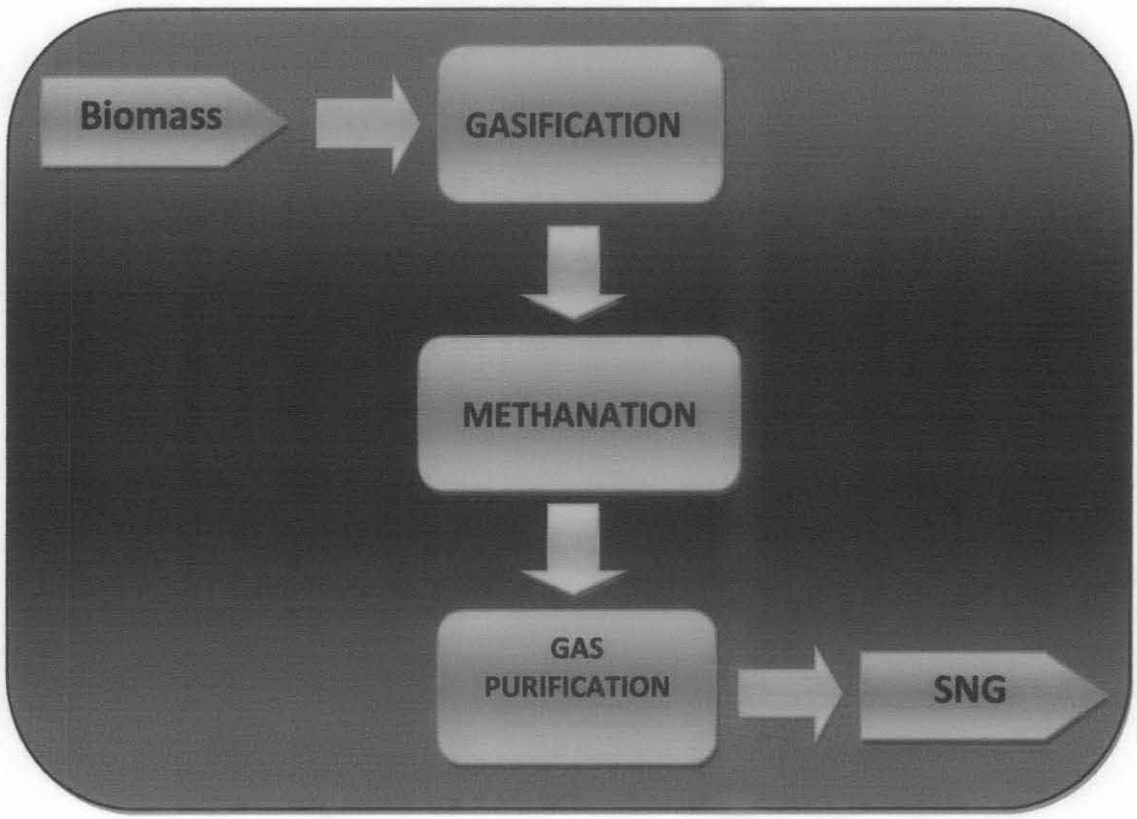

Figure 8: Block Diagram for SNG Production

In my research that I have done, SNG will be produced from the biomass or wood precisely. The conversion chain leading from wood to SNG proceeds through three steps. Wood is first gasified into a mixture mostly made of hydrogen (H2), carbon monoxide (CO), carbon dioxide (CO2) and methane (CH4) and then it is go through the conditioning part. This syngas is then further converted in a catalyzed Methanation reactor and the final methane rich gas is purified. The first step of the process is endothermic; the second is exothermic while the third is approximately neutral in terms of heat. The process design and integration will therefore play a major role in the performances of the whole conversion process.

Step 1: Gasification Process

There are several different gasification techniques commercially available and they are usually sorted into two groups; direct and indirect. In direct gasification the energy required for gasification is supplied in the same reactor by oxidising part of the feedstock. Indirect gasifiers supply energy to the reactions from an external source such as a burner. Indirect gasifiers are known to produce gases with higher methane content than direct gasifiers. Most gasifiers were however engineered to gasify coal and as a result not all techniques have a commercially available full-scale solution for biomass. Prior to gasification the feedstock needs to be pre-treated with drying and grinding. The extent of the pre-treatment depends on the gasifier in use. The gasification process produces gas from woods by heating them under carefully controlled temperature, pressure and atmospheric condition. The gasifier is heart of the gasification process. According to Synthetic Fuels Handbook by James G. Speight there are several type gasifier that can be used in gasification process such as Fixed bed Counter Current Gasifier, downdraft gasifier, oxygen–blown atmospheric or pressurized circulating bed gasifier and also bed type reactor.

Fixed bed Counter Current Gasifier is the simplest type of the gasifer. The biomass is fed at the top of the reactor and moves downward. The air is flow from the bottom and the gas leaves at the top. As a result of conversion of the biomass, the ash is removed at the bottom. The biomass moves in the counter current to the gas flow and passes through the drying zone, the distillation zone, reduction zone and the oxidation zone. The advantage of the this type of gasifier are its simplicity, high-charcoal burnt-out, and internal heat exchange leading to low gas exit temperatures and high gasification efficiency. In this way also fuel with high moisture content (up to 50% by weight) can be used. Major drawbacks are the high amount of tar and pyrolysis product, because the pyrolysis gas did not lead through the oxidation zone.

For the Downdraft Gasifier, biomass is fed at the top of the reactor and air intake is at the top or from sides. The gas leaves at the bottom of the reactor, so the fuel and gas is move in the same direction. The pyrolysis gases are lead through the oxidation zone (with high temperature) and or more or less burnt or cracked. The advantage of this gasification process is produce gas has low tar content. However the disadvantage of the gasifier is:

I. The high amount of ash and dust in the gas.
II. Inability to operate on a number of unprocessed fuels, often pellezation or briquetting of the biomass is necessary.
III. The outlet gas has high temperature leading to lower gasification industry.
IV. The moisture content of the biomass must be less 25% by weight.

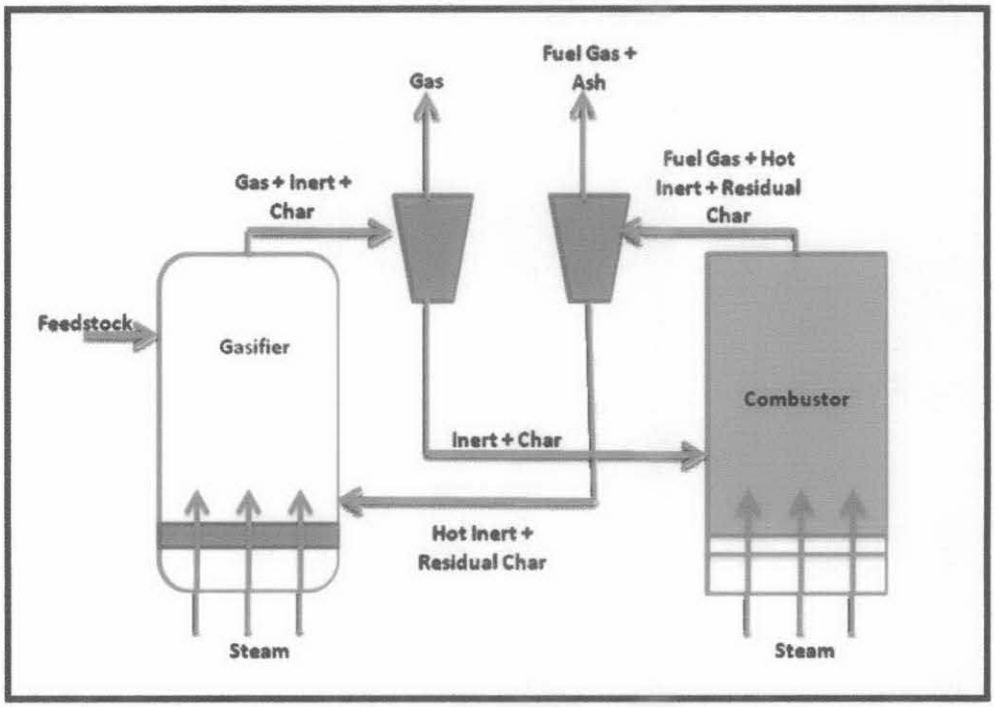

Figure 9: Pressurized circulating fluidized bed gasifier

However, when dealing with the biomass, the most suitable type of gasifier is pressurized circulating fluidized bed gasifier. This kinds of gasifiers do not encounter limitations in scaling and are more flexible concerning the particle size of fuel. This gasifying concept reduce significantly the amount of nitrogen in the product gas. By using this reactor, the nitrogen ends up in the flue gas, but not in the product gas, because gasification and combustion are separated. The energy for the gasifier is obtained by burning the chars from the first gasifier in the second reactor.

For this project, wood gasification is performed using a Fast internally Circulated Fluidized Bed (FICFB) concept: an indirectly heated fluidized bed reactor also known as pressurized circulating fluidized bed gasifier as shown in figure 9 above. There are advantages using this kind of reactor which are:

I. The flexibility of heat source.
II. Producing high purity of gas (almost free of nitrogen) without has to use pure oxygen as oxidizing agent.
III. Producing gas with high heating value.

FICFB reactor consists of two zones which are combustion zone and gasification zone. In combustion zone, the char and bed material is fluidized with air, in which wood residue are burned to heat the bed material up to 850-900 ^{O}C. In gasification zone, the biomass is fluidized by steam in which the biomass is converted to syngas using the heat carried by the circulating bed material. The temperature of the gasification zone ranges typically from 750 ^{O}C to 800 ^{O}C. In the reactor there are several gasification reaction occur as follow:

Table 4: Gasification reactions

Reaction	Name	$\Delta_r H_1$ [kJ/mol]
$C(s) + CO_2 \rightarrow 2\,CO$	Boudouard equilibrium	+172.54
$C(s) + 2H_2 \rightarrow CH_4$	Hydrogenating gasification equilibrium	-74.91
$C(s) + H_2O \rightarrow CO + H_2$	Haterogeneous water-gas shift equilibrium	+131.38
$CH_4 + H_2O \rightarrow CO + 3H_2$	Methane Decomposition	+206.28
$CO + H_2O \rightarrow CO_2 + H_2$	Water-gas shift equilibrium	-41.16

In my project, I have drawn 3 separate flow diagrams according to their process which are gasification process, methanation process and also gas purification step. The gasification process is shown as below. The main steps of the model are the following: first, biomass (BIOMASS) and steam (STEAM) are injected in the gasification zone (PYROL) where the wood is decomposed into a solid phase and syngas. The outlet stream (F) of the gasification zone contains a solid phase and a gas phase. The solid residue is separated from the product gas in solid gas separator (SEPSG). The char (solid residue) that remains in the fluidized bed will be transferred to the combustion zone(R-

2). In the model, it is assumed that the wood conversion into char is a constant that will be identified using the heat balance and experimental data obtained with the FICFB pilot plant. The gas stream (SYNGAS) is then cooled down to 25^{O}C in the heat exchanger (E-1). The water contained in this stream is condensed and separated from the gas phase in Liq/Vap Separator (DRYING1). The dry gas obtained is then desulphurised in H_2S Removal skid (H2SREM) (adsorption on a ZnO column). The clean gas (SYNCLEAN) is then divided at the splitter (S-1) into two streams: RESYN serves as supplementary fuel in the combustion zone (R-2) and SYNG leaves the process and enters the methanation step in figure 5. Solid residue (CAR) leaving solid gas separator (SEPSG) is injected with a part of the syngas produced (RESYN) in the combustion zone (R-2) where they are burned with compressed air (AIRP). This solid residue is considered to be pure carbon. The combustion in combustion reactor (R-2) is assumed to be stoichiometric and adiabatic. The hot gases (FUME) leaving the combustion zones are cooled down in the heat exchanger (E-2) from the adiabatic temperature of combustion to the temperature of the gasification zone plus 100°C (the temperature difference of the circulating bed material between the combustion zone and the gasification zone). The combustion gases are finally cooled to 150^{O}C in a second heat exchanger (E-3).

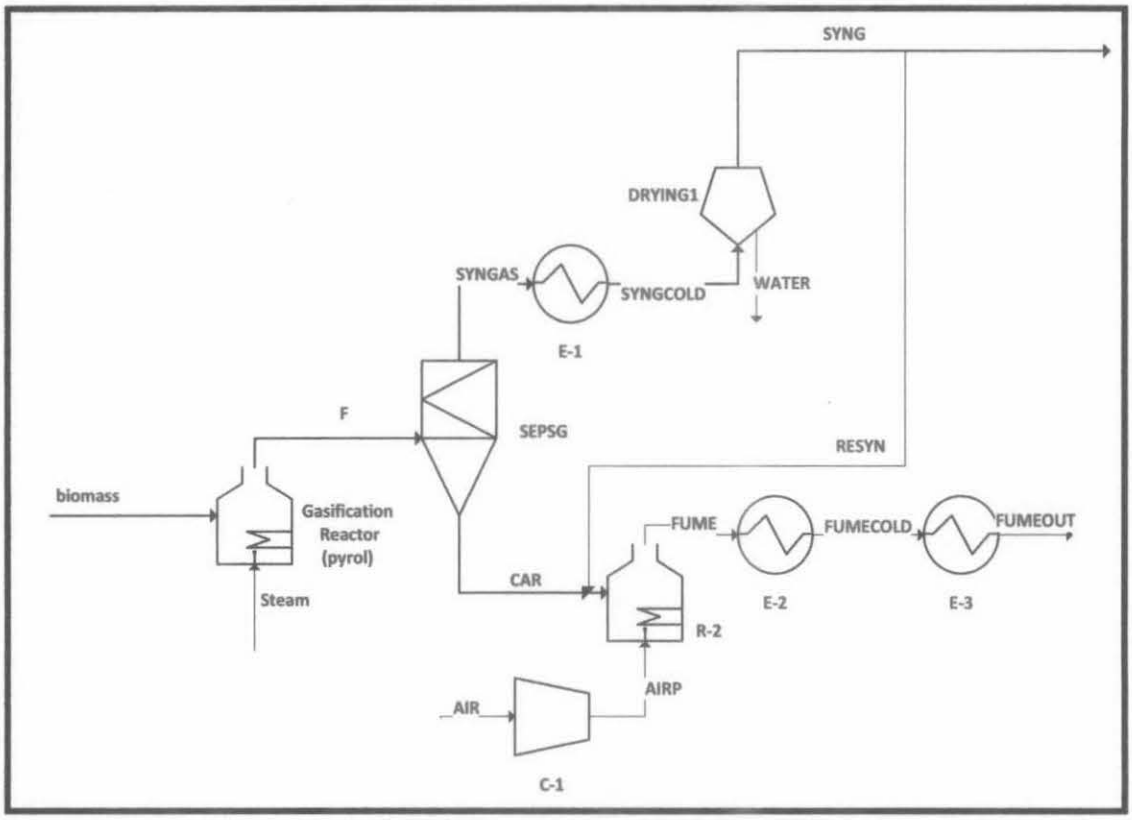

Figure 10: Gasification Process

Step 2: Methanation Step

The next crucial step in producing synthetic natural gas is Methanation step. Methanation step of converting the syngas from gasification process mainly comprises of carbon monoxide and hydrogen into methane gas and other hydrocarbon. Methanation is a catalytic process that converts syngas into methane with a nickel-based catalyst. During the Methanation process the reactions as given in the table below involve. From the heat of reaction shows, it can be seen that the Methanation process is strongly exothermic. Thus, part of the energy of these components is lost in the form of heat. Also, this heat has to be removed from the reactor efficiently. The advantage of Methanation of syngas from biomass is that at the lower temperature gasification process, some methane already forms during gasification. Methanation is a crucial part of the process and its conditions affect the overall process efficiency and also the up-stream processes of gasification and gas-cleaning.

Table 5: Methanation Reactions

Reaction	Name	$\Delta_r H_1$ [kJ/mol]
$CO + 3H_2 \rightarrow CH_4 + H_2O$	Reverse reforming reaction	-218.40
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-	-179.90
$CO + H_2O \rightarrow CO_2 + H_2$	Water-gas shift equilibrium	-37.50
$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$	Reforming reaction	+210.50

For the Methanation process the process flow diagram as follow:

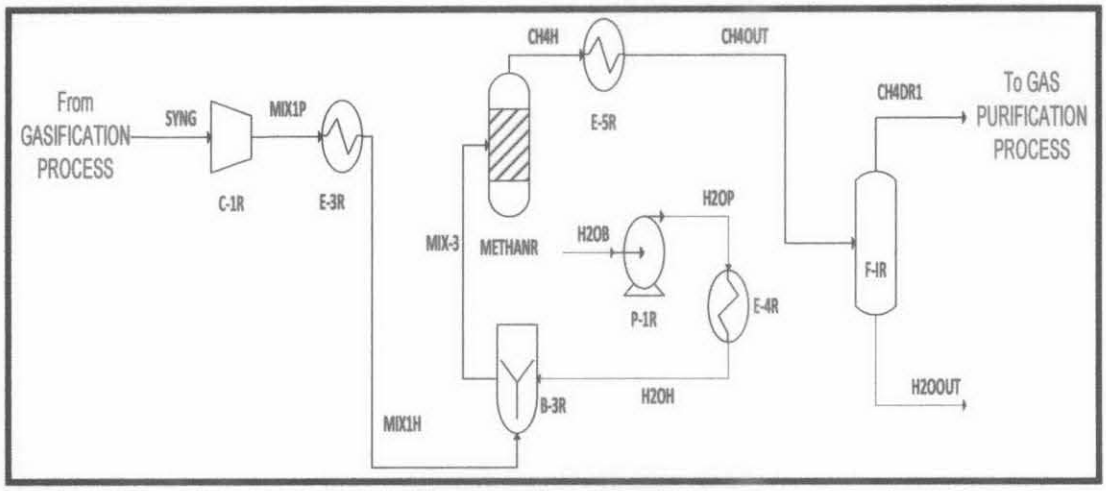

Figure 11: Methanation Process

The main steps of this model are the following: first, the syngas from the gasification unit (SYNG) is pressurized in the compressor (C-1R) to the methanation reactor pressure (60 bars). It is then preheated in the heat exchanger (E-3R) and mixed in the gas mixer (B-3R) with hot pressurized water at 200^{O}C and 60 bar (H2OH). Then, this mixture (MIX3) is injected in the fluidized bed reactor (METHANR) where the methanation reactions above take place as shown in the table 1. Only two independent chemical reactions are needed to calculate the composition of the outlet stream of the reactor since there are only seven chemical species in this stream. The gas produced (CH4H) is then cooled down in the heat exchanger (E-5R) to 30°C. The condensed water (H2OOUT) during this phase is separated in the Liq/Vap separator (F-1R) from the gas mixture (CH4DR1) leaves the process as a mixture of mostly carbon dioxide and methane and enters the purification step shown in the figure 12 below.

Step 3: Gas Purification Step

For the gasification part, briefly the purpose is to purify the methane content in which to improve its purity. To doing so, the carbon dioxide gas has to be removed from the product gas. There are a lot of carbon dioxide removal technologies existing in the world nowadays but in this process, carbon dioxide by membrane process is used. Basically, this step should removed as much as CO_2 as possible without a significant loss of CH_4 and the final concentration of CH_4 being of at least 90%. Moreover, the purification step should have low specific energy consumption. It should also be able to operate under high pressure since the pressure of the mixture coming from Methanation process is about 50-60 bar. According to all requirements above, combining 3 membranes has been chosen. This simple purification method can be operated at high pressure with a typical CH_4 recovery efficiency of 95%. The process flow diagram for Gas Purification process is shown as follow:

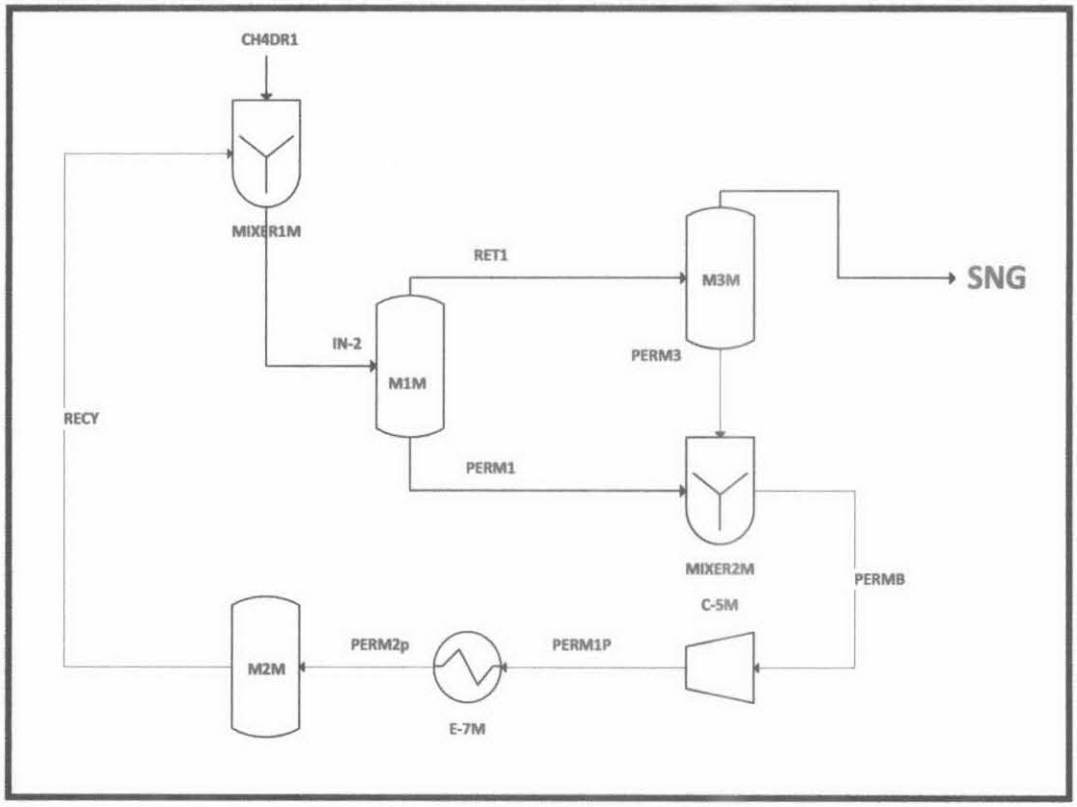

Figure 12: Gas Purification Step

The compressed, dry and desulphurised gas (CH4DR1) is first injected into membrane 1 (M1M) where it is partially enriched in methane. The retention stream (RET1), already rich in CH4, is injected into a second membrane (M3M) where it is enriched again to its final composition (SNG). To avoid an excessive loss of CH4, the corresponding permeation streams, rich in CO2 (PERM1 and PERM3), are mixed together, compressed and injected into a third membrane (M2M). The permeation stream (PERM2) coming out of this membrane leaves the process, while the retention stream rich in CH4 (RECY) returns to the inlet of the gas purification.

CHAPTER 3: METHODOLOGY / PROJECT WORK

3.1 Project Research Methodology

This project is designed to be completed in two main phases which are project research, project simulation and results evaluation. Project research is done by searching for the journal and article related, analyzing the current problems, and analyzing existing technology regarding the gas quality.

For the next phase, author has to study on every part of the process in detailed in order to find the best condition for every process. Also, take a look on the current technology applied in full-scale commercial bio-SNG plant.

3.2 Project Simulation Methodology

In this point, we come out with several process flow diagrams (PFD). From the PFD and the data given, we have to calculate mass balance manually. This mass balance is really important in order to verify the mass input is equal to mass output. The basis for this observation is the law of conservation of mass, which states that mass, can neither be created nor destroyed. So, the design of the new process is not complete until it establishes that the input and output of the entire process and of each individual unit satisfy balance equation. So, for this SNG production process, the mass balance is as follow:

3.2.1 Overall Mass Balance

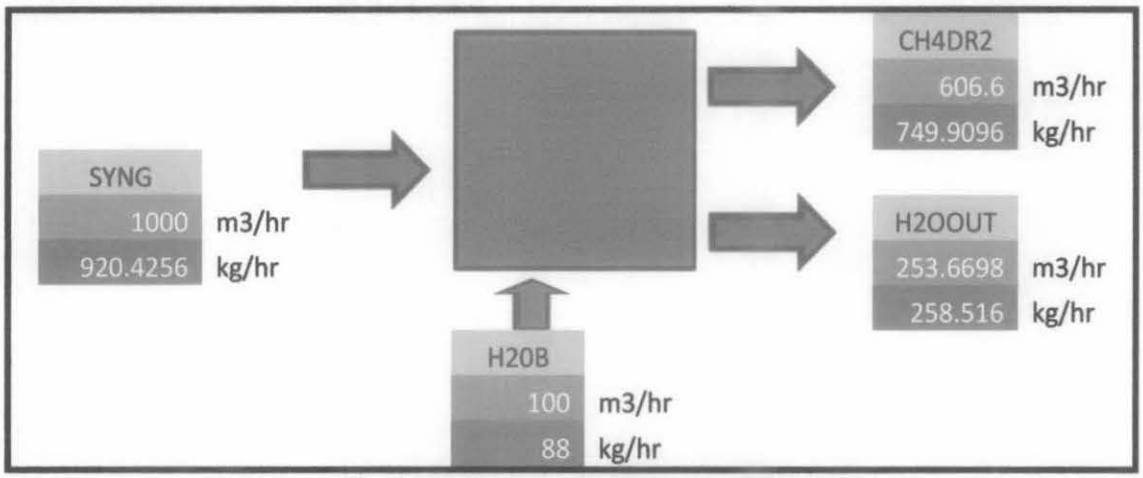

Figure 13: Overall Mass Balance Block Diagram

Table 6: Material Stream Composition

Stream	Density	SYNG			H20B		
Compound	(kg/m3)	Composition	m3/hr	kg/hr	Composition	m3/hr	kg/hr
CH4	0.55	0.11	110	60.5	0	0	0
CO	1.25	0.25	250	312.5	0	0	0
CO2	1.977	0.22	220	434.94	0	0	0
H2	0.08988	0.37	370	33.2556	0	0	0
H2O	0.88	0	0	0	1	100	88
N2	1.251	0.03	30	37.53	0	0	0
C2H4	2.085	0.02	20	41.7	0	0	0
total		1	1000	920.4256	1	100	88

Stream	Density	CH4DR2			H2OOUT2		
Compound	(kg/m3)	Composition	m3/hr	kg/hr	Composition	m3/hr	kg/hr
CH4	0.55	0.476	288.7416	158.8079	0.07	32.43201	17.84
CO	1.25	0.003	1.8198	2.27475	0.00	0	0.00
CO2	1.977	0.459	278.4294	550.4549	0.32	41.713	82.47
H2	0.08988	0.012	7.2792	0.654254	0.00	0	0.00
H2O	0.88	0.001	0.6066	0.533808	0.61	178.9048	157.44
N2	1.251	0.049	29.7234	37.18397	0.00	0.619942	0.78
C2H4	2.085	0	0	0	0.00	0	0.00
total		1	606.6	749.9096	1	253.6698	258.516

For the others 3 mass balances, will be shown in the appendices.

The diagram then will be simulating in Hysys. HYSYS is powerful software that was created by Hyprotech for simulation of chemical plants and oil refineries. It includes tools for estimation of physical properties and liquid-vapor phase equilibria, heat and material balances, and simulation of many types of chemical engineering equipment. During this simulation process, any modification of the process will be applied either in parameters such as pressure and temperature or the equipment use in order to optimize the target result.

The simulation will be shown in the result and discussion part.

CHAPTER 4: RESULT AND DISCUSSION

Production of SNG from biomass consists of 3 major processes which are gasification process, Methanation process and gas purification process. For this project, the author has focus on Methanation process which is a process of converting the syngas into methane. Figure below shows the HYSYS simulation that has been done during project simulation process. The HYSYS simulation is simulated based on PFD that has been drawn as shown in figure 14 below. For the simulation process, the HYSYS simulation process and the tables of material stream and energy stream are shown below. Before that, to simulate the simulation there are several assumption for each unit of Methanation process has been made which are:

Table 7: Assumption for each unit

Unit	Function	Parameters/Hypotheses
C-1R	Compressor	Isentropic efficeincy = 0.8 Pressure variation = 59 bar
E-3R	Heat Exchanger	No pressure drop Temperature in Mix1H =200°C
B-3R	Mixer	No pressure drop for both inlet streams
P-1R	Water Pump	Volumetric efficiency = 0.8 Pressure variation = 59 bar
E-4R	Heat Exchanger	No pressure drop Outlet Temperature (H2OH) = 200°C
METHANR	Reactor	Thermodynamic equilibrium Pressure drop = 10 bar Outlet Temperature = 400°C
E-5R	Heat Exchanger	No pressure drop Outlet Temperature = 30°C
F-1R	Liquid-Vapour Separator	No Pressure drop

Figure 14 : Hysys Simulation

Table 8: Material Stream Properties

Stream Name	SYNG	MIX1P	MIX1H	MIX3	H2OB	H2OP	H20H	CH4H	CH4OUT	CH4DR1	H2OOUT
Vapour/ Phase Fraction	1	1	1	0.968309	0	0	0	1	0.81858	1	0
Temperature [C]	25	621.3123	200	138.0304	25	25.2548	200	400	30	30	30
Pressure [kPa]	100	6000	6000	6000	100	6000	6000	5000	5000	5000	5000
Molar Flow [kgmole/h]	44.68744	44.68744	44.68744	49.57223	4.884791	4.884791	4.884791	35.92966	35.92966	29.41131	6.518351
Mass Flow [kg/h]	920.4256	920.4256	920.4256	1008.426	88	88	88	1008.418	1008.418	889.834	118.5845
Std Ideal Liq Vol Flo [m3/h]	1.768252	1.768252	1.768252	1.85643	8.82E-02	8.82E-02	8.82E-02	1.654603	1.654603	1.535369	0.119234
Molar Entalphy [kJ/ kgmole]	-121481	-99549.8	-115746	-131051	-285542	-285410	-271062	-215323	-239726	-229512	-285813
Molar Entrophy [kJ/ kgmole-C]	163.7341	168.9575	144.653	140.2935	53.29845	53.2688	90.98254	186.2535	131.4339	148.3402	55.15139
Heat Flow [kJ/h]	-5428672	-4448626	-5172408	-6496489	-1394813	-1394168	-1324081	-7736473	-8613289	-6750257	-1863032
Composition											
CH4	0.11	0.11	0.11	9.92E-02	0	0	0	0.363976	0.363976	0.444643	1.83E-07
CO	0.25	0.25	0.25	0.225365	0	0	0	1.50E-03	1.50E-03	1.83E-03	2.48E-07
CO2	0.22	0.22	0.22	0.198321	0	0	0	0.405646	0.405646	0.494037	6.82E-03
H2	0.37	0.37	0.37	0.333541	0	0	0	1.02E-02	1.02E-02	1.25E-02	1.48E-07
H2O	0	0	0	9.85E-02	1	1	1	0.181347	0.181347	1.42E-03	0.993171
N2	3.00E-02	3.00E-02	3.00E-02	2.70E-02	0	0	0	3.73E-02	3.73E-02	4.56E-02	1.26E-05
C2H4	2.00E-02	2.00E-02	2.00E-02	1.80E-02	0	0	0	6.69E-09	6.69E-09	8.17E-09	3.60E-16

Table 9: Energy Streams Properties

Name	w-1r	q-3r	w-2r	q-4r	q-MR	Q-100
Heat Flow [kJ/h]	980045.6	723781.3	644.2737	70087	-1239983	876815.9

4.1 Effect of Temperature and Pressure of Methanation Reactor

From the simulation above, the author has done some studied on the Methanation parameters towards producing amount of methane. The two parameters that has been studied is effect of temperature and pressure of Methanation process towards producing methane gas. So, the main variables studied were:

- Temperature
- Pressure

The conversion from gasification product gas to methane depends on the temperature and pressure of the Methanation. In figure 15 as shown below the concentrations of methane, carbon monoxide, hydrogen and carbon dioxide at the thermodynamic equilibrium are presented at different temperature. It is clear that at low temperatures the main products are methane and carbon dioxide, whereas at high temperature the main products are hydrogen and carbon monoxide. Due to the high exothermic character of the methanation reactions the temperature will increase significantly in adiabatic systems. Resultantly, the thermodynamic equilibrium is readily reached but with only limited conversion. To achieve high conversions the temperature must be decreased which is by removing the reaction heat. Typically, this is achieved by internally cooled reactors. The simplest system comprises a series of (adiabatic) methanation reactor with intermediate heat exchanger. The application of such a system is limited to processes at lower pressures as at higher pressures the adiabatic temperature increase in the reactors will result in too high temperatures and thermal damage of the catalysts.

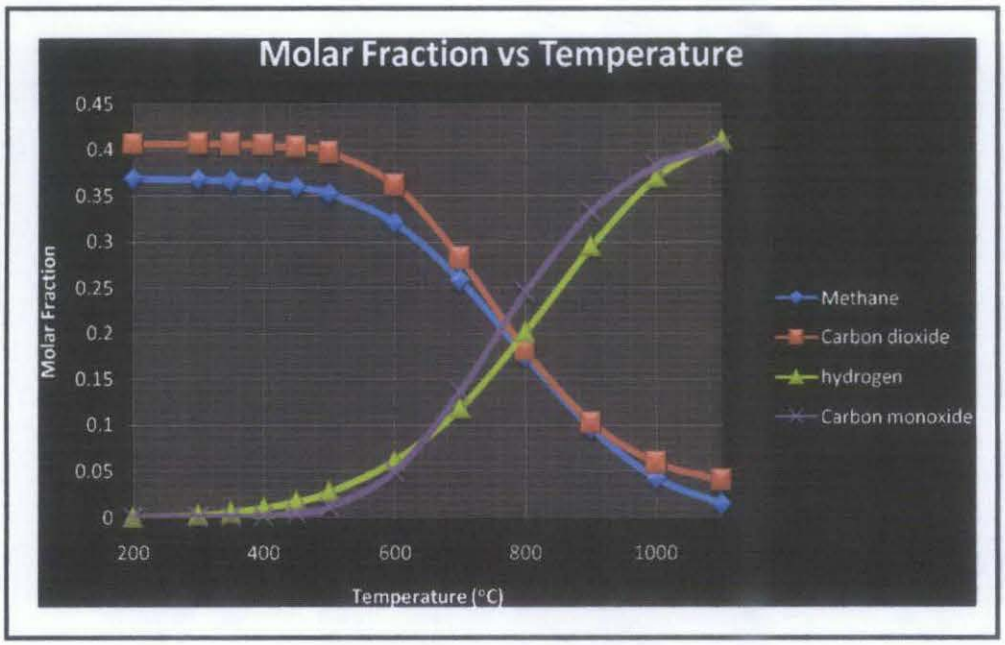

Figure 15: Graph of Molar Fraction vs Temperature

Table 10: Composition of product gas in different temperature

Compound	200°C	300°C	350°C	400°C	450°C	500°C
CH4	0.36890709	0.367890232	0.366507242	0.363975862	0.35954494	0.35202245
CO	2.68E-06	1.04E-04	4.35E-04	1.50E-03	4.41E-03	1.13E-02
CO2	0.40661527	0.40662355	0.406440855	0.405645754	0.40321216	0.3971724
H2	3.68E-04	2.61E-03	5.46E-03	1.02E-02	1.75E-02	2.80E-02
H2O	0.18658141	0.185293739	0.183736456	0.181346769	0.17820576	0.17478148
N2	3.75E-02	3.75E-02	3.74E-02	3.73E-02	3.71E-02	3.68E-02
C2H4	6.69E-13	1.34E-10	1.09E-09	6.69E-09	3.23E-08	1.26E-07
total	1	1	1	1	1	1

Compound	600	700	800	900	1000	1100
CH4	0.320598622	0.25824873	0.174461176	9.60E-02	4.20E-02	1.46E-02
CO	5.00E-02	0.13628932	0.24592092	0.333148049	0.382411206	0.404418538
CO2	0.361839335	0.28221845	0.181589104	0.102790652	5.93E-02	4.03E-02
H2	6.16E-02	0.11872726	0.201904383	0.295171222	0.370298187	0.41128334
H2O	0.170581582	0.17176549	0.166988226	0.147110886	0.122558081	0.107182468
N2	3.54E-02	3.27E-02	2.91E-02	2.57E-02	2.34E-02	2.22E-02
C2H4	1.06E-06	4.08E-06	7.80E-06	8.48E-06	5.50E-06	2.15E-06
total	1	1	1	1	1	1

The author also has done the evaluation on the effect of the different methanation reactor pressure towards the product gas getting especially to the molar fraction of the methane. For the product gas, as the pressure of the methanation reactor increase, the molar fraction or composition of methane product is increase especially. Meanwhile, the composition of carbon dioxide also increases but the composition of hydrogen and carbon monoxide slowly decreasing with increasing the pressure of the methanation reactor. So, from the graph shown that the best pressure is at 60 bar as produce more methane. At higher system pressures the thermodynamic equilibrium will shift towards higher conversion and more CH4 formation, resultantly, the adiabatic temperature increase will be higher. The conversion at 10 bar is higher compared to the system at 1 bar, thus the conversion is even higher than reactor in the 1 bar system. Furthermore, the higher pressure has an advantageous effect on the catalyst activity due to which less catalyst is required to reach the same conversion.

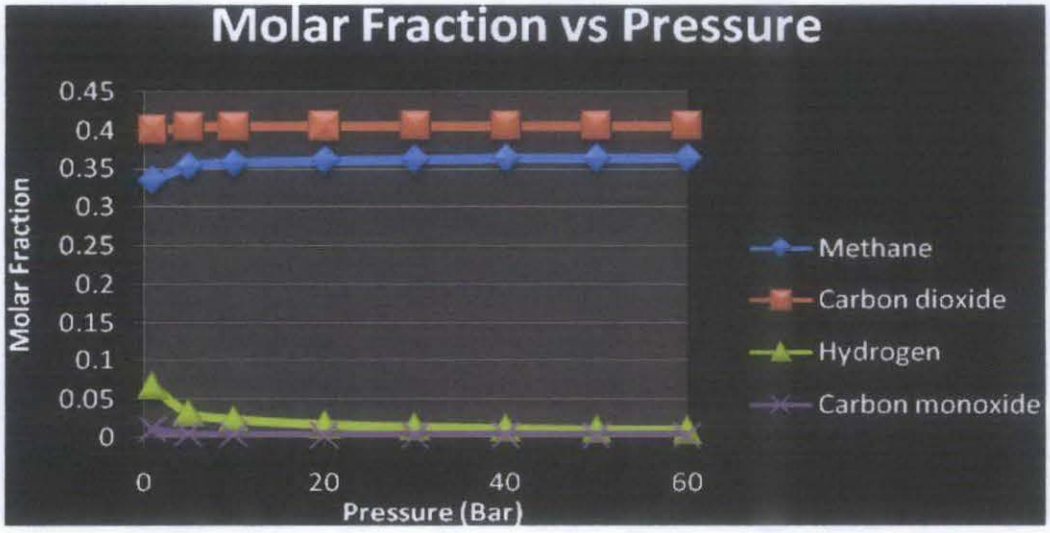

Figure 16: Graph of Molar Fraction vs Pressure

Table 11: Composition of product gas in different pressure

	Pressure (Bar)							
Compound	1	5	10	20	30	40	50	60
CH4	0.335453	0.353208	0.357721	0.360997	0.362474	0.363364	0.363976	0.36443
CO	1.01E-02	4.39E-03	3.11E-03	2.23E-03	1.86E-03	1.64E-03	1.50E-03	1.40E-03
CO2	0.40011	0.403915	0.40471	0.405234	0.405449	0.405569	0.405646	0.405698
H2	6.73E-02	3.21E-02	2.30E-02	1.63E-02	1.33E-02	1.15E-02	1.02E-02	9.27E-03
H2O	1.51E-01	1.70E-01	1.74E-01	0.178011	0.179654	0.180654	0.181347	0.181865
N2	3.61E-02	3.68E-02	3.70E-02	3.72E-02	3.72E-02	3.73E-02	3.73E-02	3.73E-02
C2H4	5.29E-09	5.24E-09	5.35E-09	5.64E-09	5.97E-09	6.32E-09	6.69E-09	7.08E-09
total	1	1	1	1	1	1	1	1

4.2 Effect of series of methanation reactor

The author also has made some evaluation study on the number of reactor contribute towards the formation of more methane. A series of two reactors has been setup to find the composition of methane at the outlet of second reactor. The product gas from the first reactor will be cooled first in the cooler to the temperature of 30°C before fed into the second reactor. The second reactor operates at 43.49 °C and once again the outlet of the reactor will be cooled until 30 °C. By having a series of methanation reactor, the composition of methane in the product gas will be increase from 36.4 % until 45.6 %.

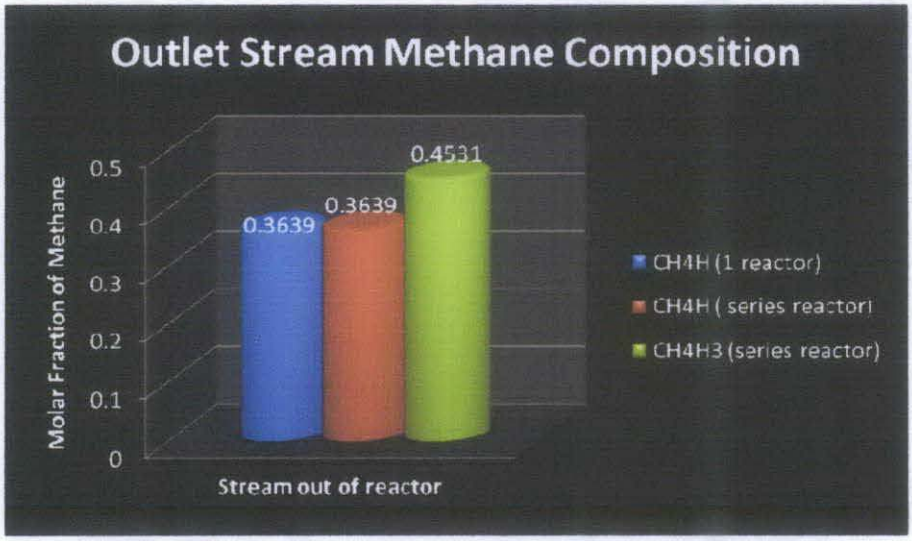

Figure 17: Outlet reactor stream methane composition

Table 12: Material Balance Properties of Series Reactor

	Only 1 Reactor			Series of Reactor			
Stream Name	CH4H	CH4OUT		CH4H	CH4H2	CH4H3	CH4H4
Vapour/ Phase Fraction	1	0.81858		1	0.81858	1	0.998621
Temperature [C]	400	30		400	30	43.49026	30
Pressure [kPa]	5000	5000		5000	5000	5000	5000
Molar Flow [kgmole/h]	35.92966	35.92966		35.92966	35.92966	29.09207	29.09207
Mass Flow [kg/h]	1008.418	1008.418		1008.418	1008.418	888.0931	888.0931
Std Ideal Liq Vol Flo [m3/h]	1.654603	1.654603		1.654603	1.65E+00	1.53E+00	1.53E+00
Molar Entalphy [kJ/ kgmole]	-215323	-239726		-215323	-239726	-231243	-231926
Molar Entrophy [kJ/ kgmole-C]	186.2535	131.4339		186.2535	131.4339	150.495	148.2879
Heat Flow [kJ/h]	-7736473	-8613289		-7736473	-8613289	-6727323	-6747221
Composition							
CH4	0.363976	0.363976		3.64E-01	0.363976	0.45314	0.45314
CO	1.50E-03	1.50E-03		1.50E-03	1.50E-03	1.60E-09	1.60E-09
CO2	0.405646	0.405646		0.405646	0.405646	0.497983	0.497983
H2	1.02E-02	1.02E-02		1.02E-02	1.02E-02	1.76E-07	1.76E-07
H2O	0.181347	0.181347		1.81E-01	0.181347	2.80E-03	2.80E-03
N2	3.73E-02	3.73E-02		3.73E-02	3.73E-02	4.61E-02	4.61E-02
C2H4	6.69E-09	6.69E-09		6.69E-09	6.69E-09	7.13E-17	7.13E-17

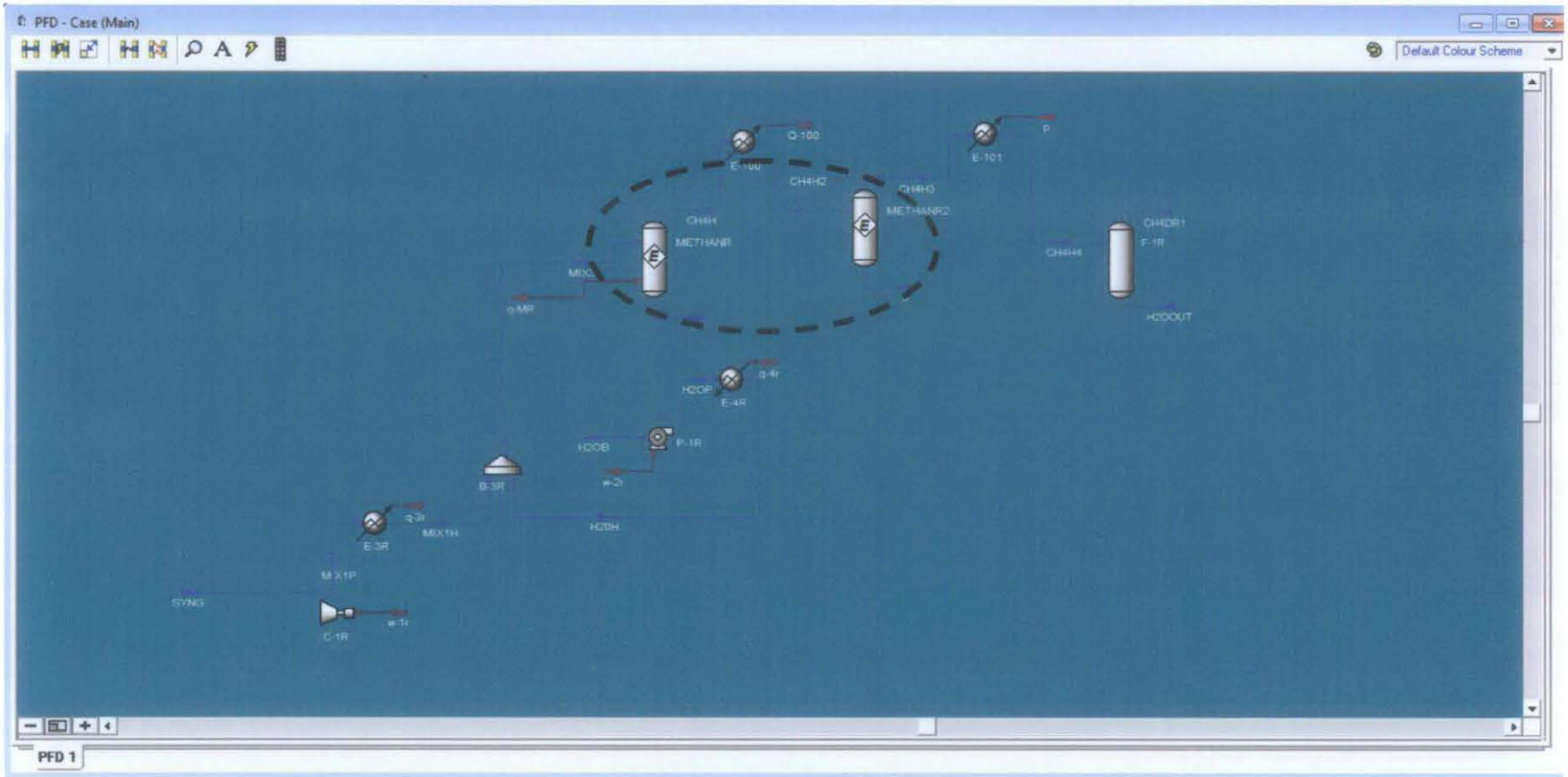

Figure 18: Hysys Simulation with series of methanation reactor

CHAPTER 5: RECOMMENDATION & CONCLUSION

As for the conclusion, the SNG production from biomass is actually a great achievement for the science world since nowadays the world needs a lot of alternative fuel to replace the fossil fuel that has been depletes. By having this SNG technology, the world gets its benefits which are not just as a fuel to cover the shortfall of fossil fuel but it is also a environmental friendly fuel.

The main objective of the project which is to evaluate the synthetic natural gas from biomass is achieved. The authors also successfully evaluate the existing technology of synthetic natural gas which is focusing on methanation process. SNG production plant from biomass consists of 3 main process which are gasification process, methanation process and gas purification process. The author is focusing on the methanation process and evaluates the effect of pressure and temperature of methanation reactor towards producing the methane. The result shows, as temperature decrease, the process will produce more methane meanwhile as the pressure increase the methane produce will be more also. The enhancement of the existing technology regarding the gas quality also being achieved by doing the evaluation by having series of two methanation reactor instead of having just only one reactor.

For the recommendation part, the author feels in the future, evaluation studies on the gas purification should be done so that pure methane can be produced. The methanation process also should be evaluated more for example maybe there should be recycle some of the methane in order to increase the purity of the methane. Evaluation study on the economic side is also important in order to ensure that the process is a optimal solution or not.

CHAPTER 6: REFERENCE

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CHAPTER 7: APPENDICES

MIXER B-3r

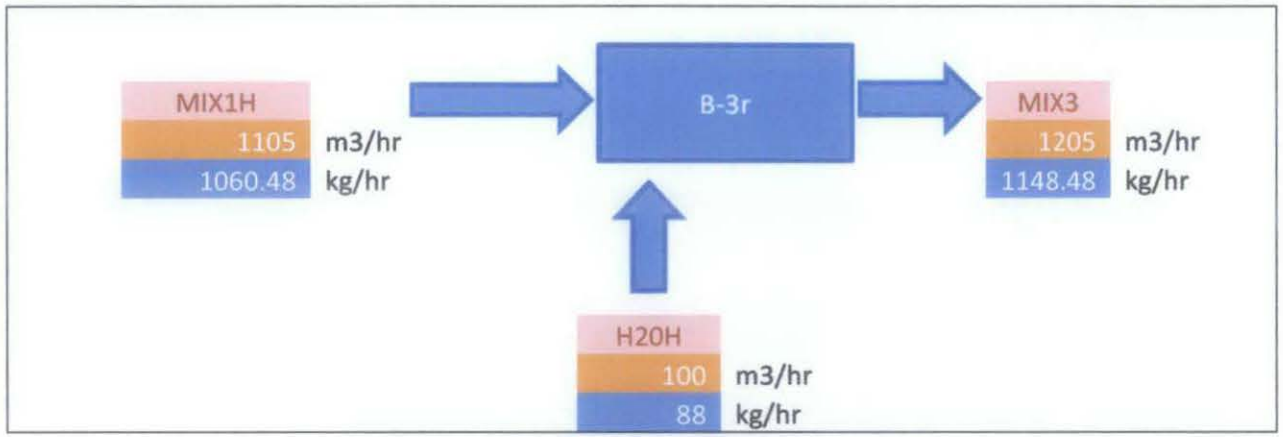

Figure 19: Mixer B-3r Block Diagram

Table 13: Material Stream Properties

Stream		MIX1H			H20H			MIX3		
Compound	Density (kg/m3)	Composition	m3/hr	kg/hr	Composition	m3/hr	kg/hr	Composition	m3/hr	kg/hr
CH4	0.55	0.139	153.595	84.47725	0	0	0	0.07	153.595	84.48
CO	1.25	0.226	249.73	312.1625	0	0	0	0.27	249.73	312.16
CO2	1.977	0.25	276.25	546.1463	0	0	0	0.48	276.25	546.15
H2	0.08988	0.336	371.28	33.37065	0	0	0	0.03	371.28	33.37
H2O	0.88	0	0	0	1	100	88	0.08	100	88.00
N2	1.251	0.031	34.255	42.85301	0	0	0	0.04	34.255	42.85
C2H4	2.085	0.018	19.89	41.47065	0	0	0	0.04	19.89	41.47
total		1	1105	1060.48	1	100	88	1	1205	1148.48

METHANATION REACTOR [METHANR]

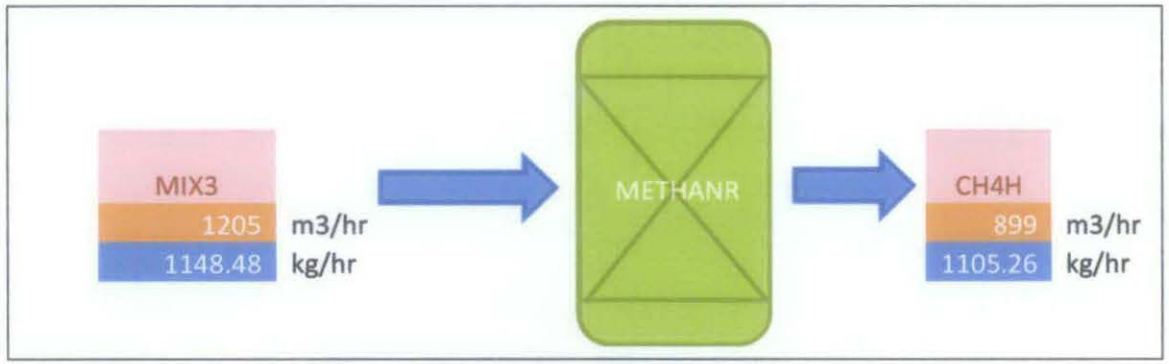

Figure 20: METHANR block diagram

Table 14: Material Stream Properties

Stream		MIX3			CH4H		
Compound	Density (kg/m3)	Composition	m3/hr	kg/hr	Composition	m3/hr	kg/hr
CH4	0.55	0.07	153.595	84.48	0.374	336.226	184.9243
CO	1.25	0.27	249.73	312.16	0.002	1.798	2.2475
CO2	1.977	0.48	276.25	546.15	0.424	381.176	753.585
H2	0.08988	0.03	371.28	33.37	0.009	8.091	0.727219
H2O	0.88	0.08	100	88.00	0.153	137.547	121.0414
N2	1.251	0.04	34.255	42.85	0.038	34.162	42.73666
C2H4	2.085	0.04	19.89	41.47	0	0	0
total		1	1205	1148.48	1	899	1105.262

LIQUID VAPOUR SEPARATOR [F-1R]

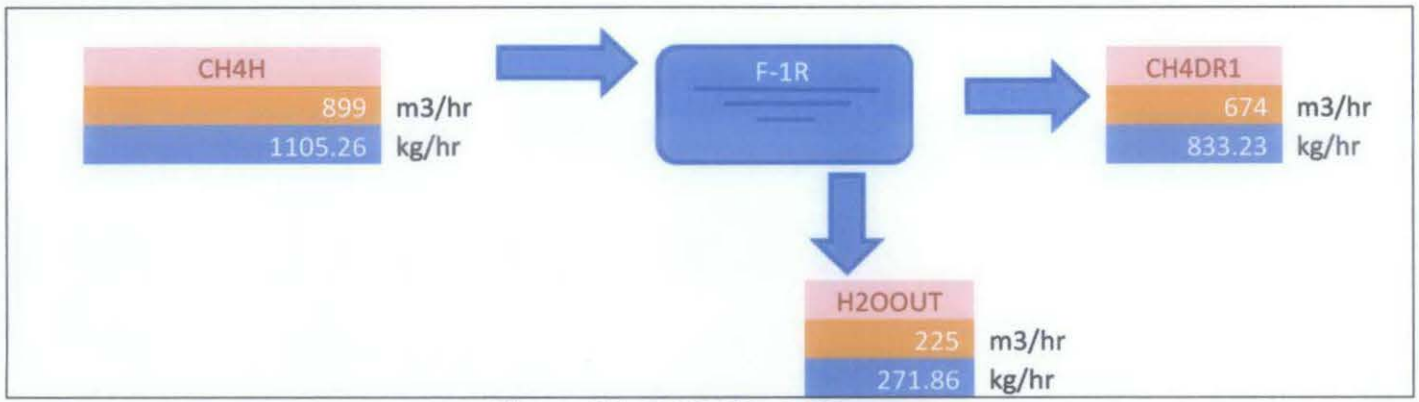

Figure 21: F-1R Block Diagram

Table 15: Material Stream Properties

Stream		CH4H			H2OOUT			CH4DR1		
Compound	Density vapor (kg/m3)	Composition	m3/hr	kg/hr	Composition	m3/hr	kg/hr	Composition	m3/hr	kg/hr
CH4	0.55	0.374	336.226	184.9243	0.07	15.525	8.54	0.476	320.824	176.45
CO	1.25	0.002	1.798	2.2475	0.00	0	0.00	0.003	2.022	2.53
CO2	1.977	0.424	381.176	753.585	0.32	71.775	141.90	0.459	309.366	611.62
H2	0.08988	0.009	8.091	0.727219	0.00	0	0.00	0.012	8.088	0.73
H2O	0.88	0.153	137.547	121.0414	0.61	137.025	120.58	0.001	0.674	0.59
N2	1.251	0.038	34.162	42.73666	0.00	0.675	0.84	0.049	33.026	41.32
C2H4	2.085	0	0	0	0.00	0	0.00	0.000	0	0.00
total		1	899	1105.262	1	225	271.86	1	674	833.23